

534

# Infrared Absorption Spectra of Some Hydroperoxides, Peroxides, and Related Compounds

O. D. SHREVE AND M. R. HEETHER, *E. I. du Pont de Nemours & Co., Inc.*, AND  
H. B. KNIGHT AND DANIEL SWERN, *Eastern Regional Research Laboratory, Philadelphia, Pa.*

The formation of peroxidic substances during autoxidation of unsaturated materials derived from fats and other substances has long been known, but their structure, quantity, and mechanisms of formation have not been adequately established. Infrared absorption spectra of a series of pure hydroperoxides, peroxides, and related compounds from 2 to 15 microns have been obtained and interpreted. On the basis of empirical analysis of the spectra of the hydroperoxides and their parent compounds it has been tentatively concluded that the hydroperoxide group gives rise to a characteristic absorption band near 12 microns. Study of the spectra of peroxides indicates that the peroxide linkage probably gives rise to a strong absorption band in the 10- to 12-micron region, but the frequency corresponding to this band is sensitive to changes in the structure of the groups attached to the peroxide linkage. The spectra are primarily intended to serve as reference data in the application of infrared spectrophotometric methods to the analyses of autoxidation mixtures.

THE formation of peroxidic substances during the reaction of unsaturated materials with oxygen has been known for a long time, but the structure of these reaction products, as well as the mechanism of their formation, has not been completely established. Originally, it was proposed that all the oxygen combined directly with the double bond, yielding a product which was saturated and contained some kind of cyclic peroxide structure (9-13). The recent isolation from oxidized nonconjugated olefins of pure  $\alpha$ -methylene hydroperoxides, in which the double bond was still intact (7, 17, 18, 21), suggested to some investigators that hydroperoxides must be the initial products of oxidation. Consideration of the high energy requirements for hydroperoxide formation, however, coupled with the fact that conjugated compounds containing  $\alpha$ -methylene groups autoxidize by addition of oxygen at the double bond, prompted Farmer (14-16) to suggest that autoxidation of olefins is universally initiated by addition of oxygen at the double bond of a few molecules only, forming free radicals. Subsequent reaction occurs by chain reactions in which the free radicals attack the  $\alpha$ -methylene position. In contrast to this, Hilditch and co-workers (2, 20) have reported that at 20° peroxidation of methyl oleate occurs to a large extent at  $\alpha$ -methylene groups, whereas at significantly

higher temperatures double bond attack predominates. Bolland and Hughes (5), however, have reported that in the autoxidation of the polyolefin, squalene, two of the oxygen atoms form a hydroperoxide group and the remaining two form an intramolecular peroxide ring.

These differences in opinion have prompted the authors to consider the use of a physical method in studying the nature of the peroxidic substances formed during the initial stage of oxidation. The main advantage of a physical method in oxidation studies would be the possibility of eliminating the need for isolating labile substances present only in small amounts.

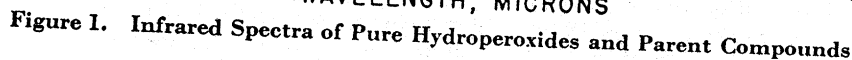
In a relatively short time, infrared spectroscopy has achieved marked success in the qualitative and quantitative determination of oxygen-containing functional groups, in a large number of both short-chain and long-chain compounds (1, 3, 4, 24, 25). The literature on organic peroxides, however, is extremely sparse, and in only a few isolated cases has infrared spectroscopy been employed in oxidation studies (6, 8, 19, 22). In these investigations, however, no report was made of the use of infrared techniques in determining the nature of the peroxidic substances formed.

from 2 to 15 microns. Interpretation of the spectra is given in the discussion.

**Spectrophotometer.** The spectrophotometer and the technique for obtaining the spectra have been described (24). All compounds which were liquid at room temperature were examined.

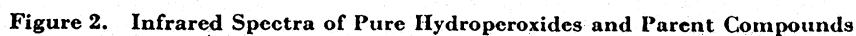
Tetralin hydroperoxide, a solid, was run as a 10% solution in carbon disulfide. Benzoyl peroxide, whose solubility in carbon disulfide is comparatively low, was run as an approximately 4% solution.

**Materials Used.** Tetralin; Tetralin hydroperoxide, melting point 54.0–54.5°; cumene hydroperoxide, boiling point 65° at 0.1 mm. and  $n_D^{25}$  1.5221; cyclohexene; cyclohexene hydroperoxide, boiling point 40–41° at 0.2 mm. and  $n_D^{25}$  1.4892; *tert*-butyl hydroperoxide, boiling point 34.5–35° at 13 mm. and  $n_D^{25}$  1.3987; and *di-tert*-butyl peroxide, boiling point 38.3° at 51 mm. and  $n_D^{25}$  1.3865, were prepared as described in a previous publication (23). Cumene (isopropylbenzene), boiling point 152° and  $n_D^{25}$  1.4910, and *tert*-butyl alcohol, boiling point 82° at 748 mm. and  $n_D^{25}$  1.3878, were obtained by efficient fractional distillation of the purest commercial grades. Benzoyl peroxide was the purest commercial grade and was used as received. Methyl oleate hydroperoxide (purity 69%) was supplied by C. E. Swift of the Southern Regional Research Laboratory.



The spectra of the four pure hydroperoxides studied (*tert*-butyl hydroperoxide, cyclohexene hydroperoxide, Tetralin hydroperoxide, and cumene hydroperoxide) and those of the parent compounds from which they are derived are shown in Figures 1 and 2. Figure 3 shows the spectra of two pure peroxides. Sample form is indicated in the lower right-hand corner and exact wave-length positions of absorption maxima are indicated on each curve.

**Common Absorption Bands Attributable to Vibrations of Hydroperoxide Group.** Because of the importance of hydroperoxides in studies of oxidation mechanisms, it is of primary interest to examine the spectra of Figures 1 and 2 for absorption bands which might be related to vibrations of the O—O—H (hydroperoxide) linkage. All bands in an infrared spectrum arise from vibrations of the molecule as a



whole, and it is not strictly correct to think in terms of vibrations of a particular linkage within the molecule. Nevertheless, it is a well-known empirically established fact that many functional groups and specific structural units do give rise to bands whose frequencies are substantially independent of the structure of the remainder of the molecule. One band whose wave-length position can almost always be relied on to remain nearly constant with change in molecular structure is that due to O—H stretching vibration. As expected, all four hydroperoxides exhibit this band near 2.8 microns. Comparison with the *tert*-butyl alcohol spectrum indicates no appreciable difference between the hydroperoxidic and the alcoholic O—H stretching frequency. Dilution with carbon disulfide shifts the O—H absorption maximum to shorter wave length in both cases, indicating considerable hydrogen bonding in the condensed state.

In attempting to select an absorption band that might be attributed to vibrations within the hydroperoxide group, or vibrations of that group moving as a unit, it seems best to consider first the spectrum of *tert*-butyl hydroperoxide in relation to that of its parent compound, *tert*-butyl alcohol. These compounds differ only in the substitution of O—O—H for O—H in the molecule, and their spectra are less complex than those of the other compounds of Figures 1 and 2. The following bands which appear in both spectra can be assigned with reasonable certainty as indicated: a band near 2.8 microns due to O—H stretching; bands near 3.3 and 6.8 microns due to C—H stretching and bending respectively; a band near 7.3 microns related to symmetrical deformation vibrations of the methyl groups (3, 26); and two bands at 8 and 8.4 microns related to vibrations of the *tert*-butyl structure (4, 26). The two bands at 9.8 and 13.4 microns are of uncertain origin, but both are present in both spectra. Thus, the only marked consequence of replacing O—H by O—O—H in this case is the disappearance of the strong band at 11 microns

(possibly related to OH bending motions in the  $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$ —OH structure) and the appearance of two new bands, a weak one near 11.3 and a strong one near 11.8 microns. From this it is concluded that if a band exists between 2 and 15 microns (other than the O—H stretching band) which can be attributed to a vibration within the hydroperoxide group (or of that group moving as a unit), the 11.3- and 11.8-micron bands represent the only possibilities. Because bands arising from vibrations of oxygenated groups are usually strong, the strong 11.8-micron band is the most likely choice.

Having thus established a limited spectral region as a definite possibility, it is now of interest to examine the spectra of the remaining three hydroperoxides in relation to those of their parent compounds in the vicinity of 11.8 microns. On so doing it is found that each of the three does indeed exhibit an absorption band near 12 microns which is absent in the corresponding parent compound.

The argument for assigning the band near 12 microns to a vibration of the O—O—H group is strengthened on further consideration of the cumene and cumene hydroperoxide spectra.

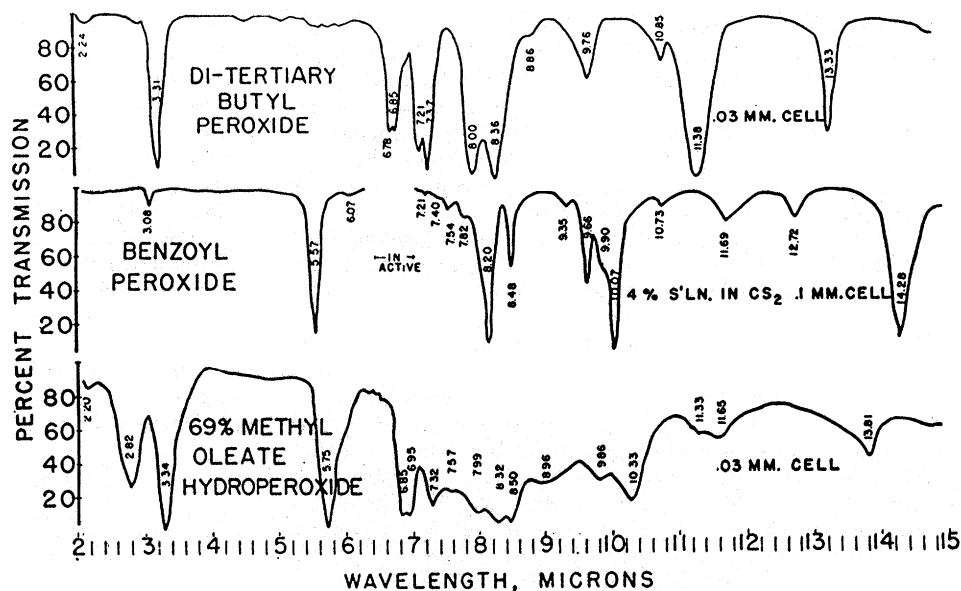


Figure 3. Infrared Spectra of Two Pure Peroxides

In general, the introduction of a substituent into a ring compound brings about marked changes in the spectrum. Because the preparation of cyclohexene and Tetralin hydroperoxides involves the introduction of O—O—H group into a ring, the spectra of these compounds do not retain many of the spectral features characteristic of the parent compounds. In the case of cumene hydroperoxide, however, no new substituent has entered the ring and most of the spectral features of the parent cumene persist in the hydroperoxide spectrum, although some wave-length shifts and changes in intensity are apparent. The following bands which appear in the cumene spectrum are usually observed at approximately comparable wave lengths in a variety of mono-substituted aromatic compounds: the strong bands at 13.2 and 14.3 microns associated with the benzenoid structure; sharp bands near 9.3 and 9.8 microns; two bands near 6.2 and 6.7 microns; the 3.3- and 6.9-micron bands; and the doublet near 7.2 and 7.4 microns. The last bands mentioned are related to C—H stretching, C—H bending, and methyl group deformation, respectively. The additional sharp band seen in the 9- to 10-micron region (near 9.6) may possibly be related to vibrations of the isopropyl group in this compound, although a shorter wave-length range has been assigned to vibrations of this group (4, 26). All these bands persist in the cumene hydroperoxide spectrum, if it can be assumed that the 9- and 9.3-micron bands in the hydroperoxide represent the 9.2- and 9.6-micron bands shifted to somewhat shorter wave length and that the 6.2-micron band has merely undergone a decrease in intensity. Thus it would seem that all but three of the strong bands in the cumene hydroperoxide spectrum can probably be assigned to various vibrations of the cumene residue in the molecule. This leaves three strong bands to account for. Of these three, the two at 7.9 and 8.7 microns (unlike the 12-micron band) are not common to all four hydroperoxides. This leaves the strong 12-micron band as the most probable assignment to a vibration involving the peroxide linkage in the O—O—H group or possibly a bending motion of the hydroperoxide group as a unit.

Because of the complications incident to ring substitution, the assignment of the 12-micron band to a vibration of the hydroperoxide group in cyclohexene hydroperoxide and Tetralin hydroperoxide is less certain. However, in view of the above arguments for the probable reliability of the assignment in the cases of *tert*-butyl and cumene hydroperoxides, together with the fact that the band does appear in all four cases, the authors have tentatively concluded that the presence of the hydroperoxide

group in an organic molecule gives rise to an absorption band in the vicinity of 12 microns.

Aside from the assignments already mentioned, no further interpretation of the complex cyclohexene and Tetralin hydroperoxide spectra will be attempted. One interesting feature of the cyclohexene hydroperoxide spectrum, however, should be noted. While the 6-micron  $C=C$  stretching band in the cyclohexene spectrum is only moderately strong, the intensity of this absorption in cyclohexene hydroperoxide has been greatly enhanced. The change in molecular symmetry resulting from substitution of the  $O-O-H$  group on a carbon adjacent to the double bond has evidently brought about a marked increase in the infrared activity of this vibration.

Included in Figure 3 is an absorption curve run on methyl oleate hydroperoxide (purity 69%). The broad absorption near 11.7 microns represents a considerable increase over that observed in the spectrum of a sample of pure methyl oleate. Some of this increased absorption probably arises from the hydroperoxide groups present, but conclusions on this point must await the availability of a pure sample of methyl oleate hydroperoxide, which the authors are now attempting to prepare. The failure to observe a stronger increase in absorption in the 12-micron region than was actually obtained might seem surprising. It has been observed, however, in studies (24, 25) of other oxygenated long-chain compounds containing oxirane and hydroxy groups, that in the liquid or solution state the absorption bands attributable to these oxygen-containing groups are broad and weak, whereas in the solid state they are sharp and intense. This suggests that infrared spectra of mixtures of oxidation products be determined at low temperatures in the solid state to bring out bands which are broad and weak in the liquid state. The strong  $O-H$  stretching band near 2.8 microns arises from hydroperoxidic hydroxyl and other types of hydroxyl groups present in this complex mixture. The strong band at 10.36 microns (not present in methyl oleate) is characteristic of *trans*-octadecenoic acids and esters, thus indicating that geometric isomers may be formed under the oxidizing conditions employed in preparing this mixture from methyl oleate.

#### PEROXIDES

Only two pure peroxides were available for study at the time of this report. Their spectra are shown in Figure 3.

**Di-*tert*-Butyl Peroxide.** The spectrum of this compound bears a strong over-all resemblance to those of *tert*-butyl alcohol and *tert*-butyl hydroperoxide. From the discussion of the latter two spectra it will be clear that all bands in the di-*tert*-butyl peroxide spectrum can probably be attributed to vibrations of the alkyl residues, with the exception of the strong band near 11.4 microns and the very weak band at 11 microns. Thus by reasoning similar to that employed in the analysis of the *tert*-butyl hydroperoxide spectrum it may be concluded that the 11.4-micron band is the only band that could possibly be related to vibrations of the peroxide linkage in this molecule.

**Benzoyl Peroxide.** Although, in view of the above, this compound might have been expected to show an absorption band near 11.4 microns, no such band is present. In the benzoyl peroxide spectrum only three strong bands occur in the longer wave-length region. That at 14.3 microns is related to vibrations of the phenyl ring (4, 26) and that at 8 microns is very likely related to a  $C=O$  stretching vibration (4, 24-26). If, therefore, any band is assignable at the present time to a vibration of the peroxide linkage, the 10-micron band represents the most probable choice. Thus if the highly tentative assignment of the 11.4-micron band in di-*tert*-butyl peroxide and the 10-micron band in benzoyl peroxide to a vibration of the  $O-O$  linkage is correct in both cases, the vibration frequency involved must be sensitive to changes in the structure of the two groups attached to the  $O-O$  linkage. Although the authors have not yet studied additional pure peroxides, infrared spectra of several additional peroxides

(some claimed to be pure and others of uncertain purity) are included in a commercially available catalog of spectra. Examination of these spectra reveals the interesting fact that those containing aryl groups attached to the peroxide linkage (phthaloyl peroxide, *p*-chlorobenzoyl peroxide, and benzaldehyde peroxide) all show a strong band near 10 microns in common with that observed in benzoyl peroxide. Two acyl-type peroxides in this file show common absorption near 9.4 microns. Several others containing widely variable substituent groups show no common band that could be attributed to a vibration of the peroxide linkage.

From these observations, it seems likely that absorption due to the peroxide linkage will vary widely with the nature of the attached groups. In view of the existence of a common band (10 microns) in the four aryl peroxides mentioned above, however, it may be possible to assign a fairly narrow wave-length range to this type of vibration in each of several classes of peroxides whose individual members are closely related.

#### COMMENTS AND CONCLUSIONS

The potentialities of the infrared method as applied to any type of chemical problem cannot be assessed until spectra of appropriate pure compounds are available for reference. Thus the spectra presented here should be useful in connection with the possible application of this method to a wide variety of problems involving peroxides and hydroperoxides. When sufficient reference spectra of this type are available, it may be possible to distinguish various types of peroxide compounds involved in oxidation and other studies and to determine one type in the presence of others by this physical method of analysis.

#### ACKNOWLEDGMENT

The authors are grateful to R. E. Koos of the Eastern Regional Research Laboratory for the preparation and analysis of some of the reference compounds, and to C. E. Swift of the Southern Regional Research Laboratory for the methyl oleate hydroperoxide (purity 69%).

#### LITERATURE CITED

- (1) Anderson, J. A., and Seyfried, W. D., *ANAL. CHEM.*, **20**, 998 (1948).
- (2) Atherton, D., and Hilditch, T. P., *J. Chem. Soc.*, **1944**, 105.
- (3) Barnes, R. B., Gore, R. C., Liddel, U., and Williams, V. Z., "Infrared Spectroscopy," New York, Reinhold Publishing Corp., 1944.
- (4) Barnes, R. B., Gore, R. C., Stafford, R. W., and Williams, V. Z., *ANAL. CHEM.*, **20**, 402 (1948).
- (5) Bolland, J. L., and Hughes, H., *J. Chem. Soc.*, **1949**, 492.
- (6) Cole, J. O., and Field, J. E., *Ind. Eng. Chem.*, **39**, 174 (1947).
- (7) Criegee, R., Pilz, H., and Flygare, H., *Ber.*, **72**, 1799 (1939).
- (8) Dugan, L. R., Beadle, B. W., and Henick, A. S., *J. Am. Oil Chemists' Soc.*, **26**, 681 (1949).
- (9) Engler, C., *Ber.*, **33**, 1090 (1900).
- (10) *Ibid.*, p. 1097.
- (11) *Ibid.*, p. 1109.
- (12) Engler, C., and Weissberg, J., *Ibid.*, **31**, 3046 (1898).
- (13) Engler, C., and Wild, W., *Ibid.*, **30**, 1669 (1897).
- (14) Farmer, E. H., *J. Soc. Chem. Ind.*, **66**, 86 (1947).
- (15) Farmer, E. H., *Trans. Faraday Soc.*, **42**, 228 (1946).
- (16) Farmer, E. H., *Trans. Inst. Rubber Ind.*, **21**, 122 (1945).
- (17) Farmer, E. H., and Sundralingam, A., *J. Chem. Soc.*, **1942**, 121.
- (18) Farmer, E. H., and Sutton, D. A., *Ibid.*, **1943**, 119.
- (19) Gamble, D. L., and Barnett, C. E., *Ind. Eng. Chem.*, **32**, 375 (1940).
- (20) Gunstone, F. D., and Hilditch, T. P., *J. Chem. Soc.*, **1945**, 836.
- (21) Hock, H., and Schrader, O., *Naturwissenschaften*, **24**, 159 (1936).
- (22) Honn, F. J., Bezman, I. I., and Daubert, B. F., *J. Am. Chem. Soc.*, **71**, 812 (1949).
- (23) Knight, H. B., and Swern, D., *J. Am. Oil Chemists' Soc.*, **26**, 366 (1949).
- (24) Shreve, O. D., Heether, M. R., Knight, H. B., and Swern, D., *ANAL. CHEM.*, **22**, 1498 (1950).
- (25) *Ibid.*, **23**, 277 (1951).
- (26) Thompson, H. W., *J. Chem. Soc.*, **1948**, 328.

RECEIVED May 19, 1950. Presented before the Division of Organic Chemistry at the 177th Meeting of the AMERICAN CHEMICAL SOCIETY, Philadelphia, Pa. Report of a study in which certain phases were carried on under the Research and Marketing Act of 1946. Paper VII in the series "Reactions of Fatty Materials with Oxygen." Paper VI in (26).